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Esterification of acetic acid via semi-batch reactive distillation for pyrolysis oil upgrading: experimental approach

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Abstract

In this study, bio-oil upgrading using deoxygenation of acetic acid with heterogeneous solid catalyst via reactive distillation was studied. Two types of solid catalysts were used in the experiments comprising of acid-doped raschig ring and Amberlyst IR 120 H+. The experiments were carried out in a pilot semi-batch reactive distillation column with temperature at reboiler and condenser of around 120°C and 55°C. The experimental results showed that, operated with Amberlyst IR 120 H+, the esterification reaction reached 79.5 percent of acetic conversion and purity of methyl acetate from top stage was 72 mole percent. With acid-doped raschig ring, the purity of methyl acetate from the top stage was 68 mole percent.

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Keywords: Biomass; bio-oil; deoxygination; esterification; reactive distillation

1. Introduction

Bio-oil obtained from fast pyrolysis of biomass has been recently proposed as a renewable energy source. Bio-oil, however, is very complex in composition as they can consist of variety of components

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depending on different factors, such as pyrolysis conditions and types of biomass. It contains a large amount of oxygenated compounds categorized as group of carboxylic acids, ketones, phenols, aldehydes and water. Acetic acid is a major oxygenated compound in bio-oil, which can be found from pyrolysis of different biomass. Bio-oils can be referred to as liquid product from solid biomass via pyrolysis process. Alternative terms referring to bio-oils are biomass pyrolysis liquids, pyrolysis oils or bio-crude oils. Bio-oils are dark brown, free flowing liquid, which has smoky odor. The obtained bio-oils are very complex in composition, and contain a large amount of oxygenated compounds, such as carboxylic acids, ketones, phenols, aldehydes, water and etc. The presence of acids in bio-oil makes it highly acidic and corrosive [1]. Bio-oils may not be directly used for internal combustion engine because the high oxygenated compounds and high water content causes ignition delay and reduces combustion rates. Furthermore, bio-oils are very corrosive to engine because of its acidity. For the use of bio-oils with internal combustion engine, it is, therefore, necessary to upgrade bio-oils by reducing water, oxygenated and acidic contents.

Esterification reaction of organic acids with alcohol is a potential route for reducing acid and oxygenated contents in bio-oils by converting it to ester and water by the use of acid catalyst. In 2008 Jun Peng et al. worked on esterification reaction of bio-oil from fast pyrolysis of rice husk with ethanol and the resulted showed that total amount of acid, phenol, ketones and aldehydes in bio-oil was decreased, whereas the amount of esters increased [2]. Shaojun Miao et al. studied on esterification of acetic acid with methanol, which was investigated as a model reaction for stabilization of bio-oil. A heterogeneous catalyst mesoporous silica, SBA-15, was compared to homogeneous H_2SO_4 catalyst and it demonstrated a comparable results [3]. Jin-Jiang Wang et al. worked on upgrading bio-oil by esterification using two types of catalyst consisting of 732 and NKC-9 ion-exchange resin catalyst. The result showed that acid content in bio-oil after upgrading using 732 and NKC-9 catalyst was decreased to 88.54 and 85.95%, heating value increased 32.26 and 31.64% and moisture contents decreased 27.74 and 30.87%, respectively [4].

In this work, acetic acid was selected as a model component for reactive distillation because bio-oils are complex mixtures and acetic acid is a large carboxylic group in bio-oil from pyrolysis process and with its presence in bio-oils, acidity of the oils may be high. It was also found that acetic acid is one of the major components in bio-oils from different types of biomass at various compositions, such as, 16.8wt% from beech wood, 15.6wt% from pine, 18.5wt% from rice husk and 5.46wt% from palm kernel shell [5 – 7]. It was a large amount compared to other components in bio-oils and acetic acid is oxygenated compound that should be upgraded. Esterification reaction of acetic acid and methanol can be written as follows [8]:

$$CH_3COOH + CH_3OH \leftrightarrow CH_3COOCH_3 + H_2O \quad (1)$$

From the reaction, acetic acid and methanol are combined to form methyl acetate and water. Methyl acetate can be used as solvent for the production of coating materials, nitro-cellulose, cellulose acetate, cellulose ethers, and celluloid. It can also be used with a wide variety of resins, plasticizers, lacquers and certain fats [9].

Reactive distillation is a process that combines reaction and distillation in the same unit. The advantages of reactive distillation that can be summarized as follows [10]:

- Increase conversion of reaction because the product is continuously removed from the system. Therefore, the equilibrium of reactions may be avoided
- Save energy and cost as it combines distillation and reaction process in the same unit
- Avoidance of azeotropic distillation

Therefore, this study focused on deoxygination of acetic acid using esterification with methanol to produce methyl acetate and water as by-product. The esterification reaction of acetic and methanol is reversible reaction and in order to drive the reaction forward, the products must be removed from the reaction simultaneously. Therefore, the deoxygination reaction was carried out in a reactive distillation column, in which reaction and separation process can run at the same time and the main products can be removed and separated from the reaction via distillation process.

2. Experimental

2.1. Chemicals

In this work, acetic acid (99.85%) was purchased from Celanese (USA). Methanol (99.8%) was supplied from Merck. Sulfuric acid (98%) was purchased from Qrec and Amberlyst IR 120 H+ was purchased from Sigma-Aldrich with the moisture content in the Amberlyst IR 120 H+ of 53 – 58% and particle size of around 620 – 830µm. Raschig ring was made from ceramic with the inside and outside diameter of 15mm and 7mm respectively and the length of 15 mm. Two types of catalyst supports used in this work are shown in Fig. 1.

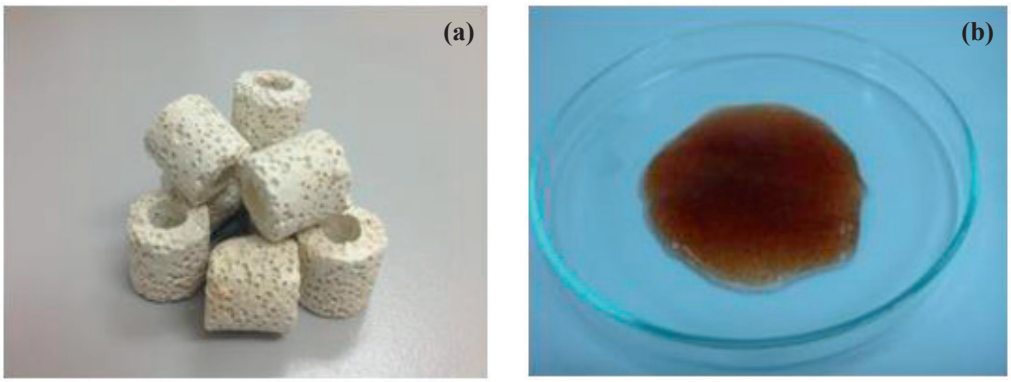

Fig. 1. Image of raschig rings (a) and image of amberlyst IR 120 H^+ used in this work

2.2. Catalysts

Two types of solid catalysts were used in the experiments. Acid-doped raschig ring was prepared by washing rough ceramic raschig ring with methanol to remove impurities and soaking with 1M sulfuric acid solution for 12h. Amberlyst IR 120 H+ was packed into sieve bags, as shown in Fig. 2, and soaked with 1M sulfuric acid solution for 12h and was then washed by distilled water. Each catalyst was packed in distillation column according to experiment set up.

Fig. 2. Sieve bags for packing Amberlyst IR 120 H^+

2.3. Reactive distillation column

The experiments were carried out in a pilot semi-batch reactive distillation column with 11.43cm diameter and seven stages including condenser and reboiler as shown in Fig 3. Two types of solid catalysts were used in the experiments comprising of acid-doped raschig ring and Amberlyst IR 120 H^+. From Fig. 3, acetic acid was fed into the reboiler, while methanol was fed at a stage above the reboiler. The reboiler was heated by ceramic band heater. At condenser, cooling water was used as cooling medium. The temperatures in the column were measured and controlled using thermocouples and PID controller.

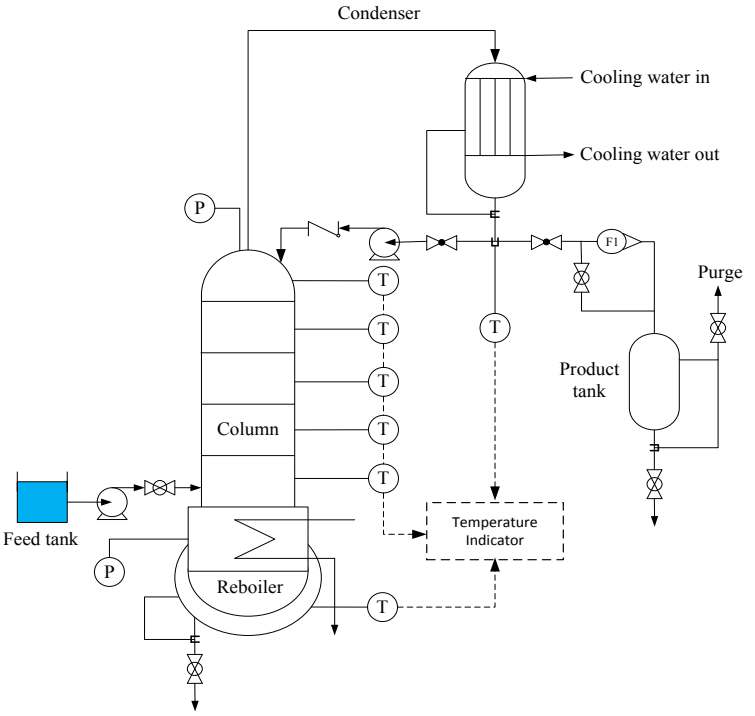

Fig. 3. Schematic diagram of reactive distillation set up

2.4. Experimental procedure

Four liters of acetic acid was fed into the reboiler and was heated from room temperature to 120°C with a heating rate of 5°C·min^{-1}. Then, three liters of methanol was fed into the column with a rate of 50 ml·min^{-1} and the reflux rate was kept constant at 100ml·min^{-1}. Once the reflux rate, pressure and temperature in the column, condenser and reboiler were steady, the first sample from the product tank and reboiler were collected and then again every five minutes. All samples were analyzed in order to measure the content of methanol and methyl acetate using gas chromatography-flame ionization detector (GC-FID, Agilent Technologies 7890A-5979C), water content using Karl-fischer (Metrohm 888 titrando) and acid content using Auto titration (Metrohm 888 titrando) with 0.1M of KOH.

3. Results and Discussions

3.1. Thermodynamic conditions in reactive distillation column before the first sample collection

Experimental results before the collection of the first sample was summarized in Table 1.

Table 1. Thermodynamic condition in the column before the first sample was withdrawn from the reboiler and product tank

	Acid–doped raschig ring	Amberlyst IR 120 H+
Temperature (°C)		
Condenser	52.6	49.6
Stage 2	80.9	63.9
Stage 3	81.8	64.2
Stage 4	82.8	65.9
Stage 5	83.1	65.9
Stage 6	94.1	67.8
Reboiler	95.5	80.7
Pressure at reboiler (barg)	1.1	1.5
Pressure at condenser (barg)	Ambient	Ambient
Reflux rate (ml·min^{-1})	141	94

3.2. Mole fraction of components and operating conditions at various operating times

Fig. 4 shows the pressure at reboiler during the experiment while the pressure at the condenser was at ambient pressure. At the beginning of the experiment, the pressure in the system was at ambient pressure and gradually increased and reached constant pressure at 1.1 and 1.5 barg for the system with raschig ring and Amberlyst respectively and the pressure in the system was relatively stable before the first sample from product tank and reboiler were withdrawn for analysis. At this point, the esterification reaction may occur and the equilibrium state of the reaction may be reached as the temperature and pressure in the system were steady. From the graph, the pressure in the system with Amberlyst was higher than the one with raschig ring, which could be because the particle size of Amberlyst was smaller than that of raschig ring and it was also packed into a sieve bags and then were installed in the column. Therefore, it resulted in higher pressure drop.

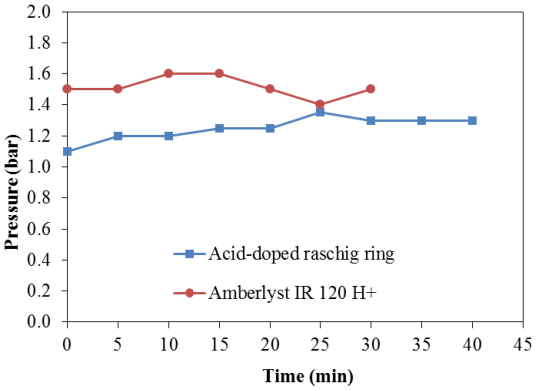

Fig. 4. Pressure at reboiler varied with times

The mole percent of samples at product tank are shown in Fig. 5 for the results from the system with raschig ring and Amberlyst, respectively. It can be seen that after the equilibrium state and the first sample was taken, methyl acetate and water, the product of the reaction were formed as can be seen from Fig. 5(a) and Fig. 5(b) at the beginning of the graphs.

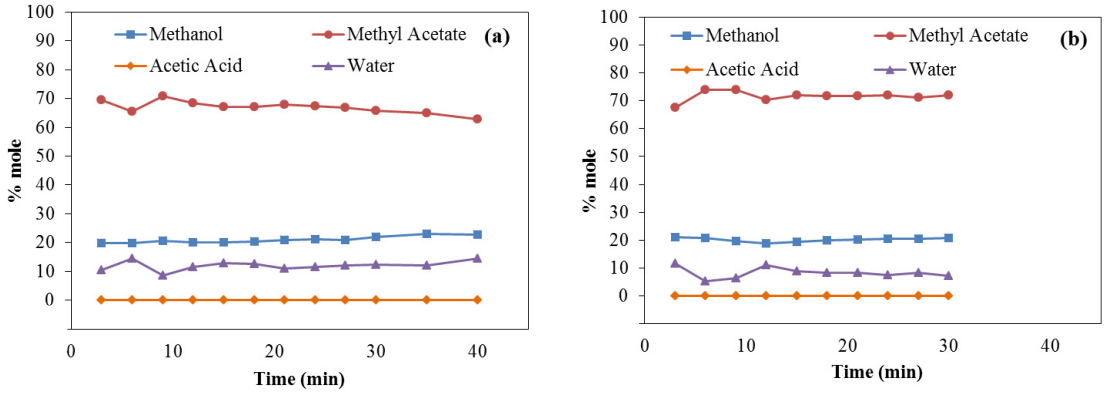

Fig. 5. Mole fraction at product tank (a) using acid-doped raschig ring catalyst; (b) using Amberlyst IR 120 H^+ catalyst

In Fig. 5(a), mole percent of methyl acetate, methanol and water are around 68, 20 and 12 respectively. It shows that reaction occurred and produced main product and by-product. The distillation could separate methyl acetate from the reactants and by-product. The presence of methanol in the product tank could be that the conversion of the reaction was not reached 1 and the boiling point of methanol, 64.7°C, was close to that of methyl acetate, 56.9°C. Therefore, the column may not be able to completely separate the two components and around 20 mole percent of methanol presented in the product tank. As for water, its content was at around 10 mole percent and could be due to the performance of separation process. Additionally, acetic acid in product tank could not be detected, which shows that the column could separate acetic acid from the products.

In Fig. 5(b), mole percent of methyl acetate, methanol and water are around 72, 20 and 8 respectively. The methyl acetate content from the system with Amberlyst was higher than that of the system with raschig ring. This may be due to two main reasons, the higher activity of the catalyst and the better

performance of separation as it can be seen that the pressure in the reboiler in Fig. 4 of the column with Amberlyst was higher, which may introduce the higher activity of the reaction.

In reboiler section, only the amount of acetic acid and water were analyzed in order to investigate the change in acid content that was consumed during the reaction and separation process. The results are shown in Fig. 6. The results in Fig. 6(a), which is from the system with raschig ring, show that the amount of acid, which was a reactant, was as high as 79 percent at the beginning before the first sample was withdrawn. At this state of the reaction, equilibrium may occur. Then, the amount of acid decreased rapidly until the certain extent, around the 17th minute corresponding to the rapid increase of the amount of water. During this time, the equilibrium of the reaction may be disturbed as methyl acetate was withdrawn from the system at the product tank. Then the reaction could be in the forward direction again. After this point, the content of acid increased. This may be due to the lower content of methanol at the reboiler and the reaction may reach a new equilibrium state, where there was very low amount of methanol, and the reaction could not go forward as it showed that the amount of water increased to 62 percent and the amount of acid was at 30 percent at the 40th minute.

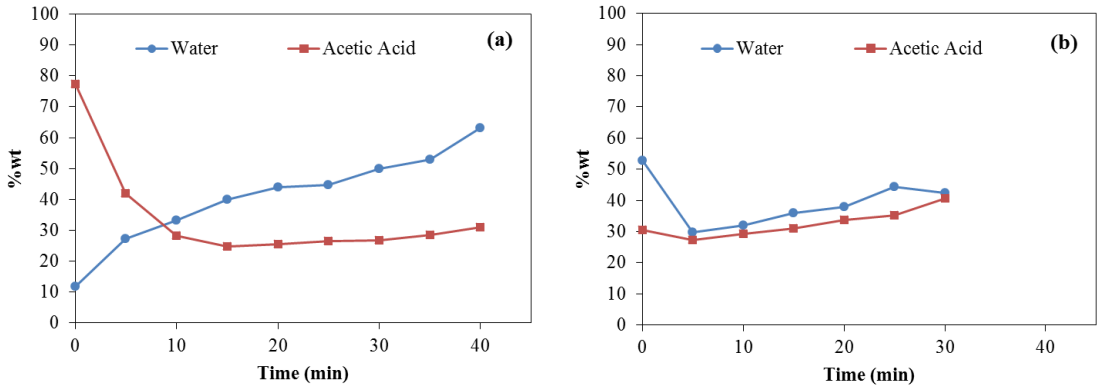

Fig. 6. Weight percent of water and acid content with time at reboiler (a) using acid-doped raschig ring catalyst; (b) using Amberlyst IR 120 H^+ catalyst

Results in Fig. 6(b), which is the results from the system with Amberlyst, also show the same trend as Fig. 6(b), in term of the change in acid and water content apart from the result at time zero, which may be due to analytical error.

The conversion of acetic acid can be calculated as the following:

$$\%\text{conversion} = \frac{\text{Initial weight of acetic acid - Final weight of acetic acid}}{\text{Initial weight of acetic acid}} \times 100 \qquad (2)$$

The esterification reaction of the experiment using Amberlyst in this study reached 79.5 percent of acetic conversion.

4. Conclusion

The experimental results showed that acetic acid can be converted by esterification reaction with methanol to produce methyl acetate using heterogeneous solid catalyst via reactive distillation. The amount of acid in reboiler decreased rapidly corresponding to the increase of the amount of water. Methyl

acetate was separated from the column at 68 and 72 mole percent from the system with acid-doped raschig ring and Amberlyst IR-120 H+, respectively. Operation with Amberlyst IR 120 H+, the esterification reaction reached 79.5 percent of acetic conversion and purity of methyl acetate from top stage was 72 mole percent, which is higher than that of acid-doped raschig ring with 68 mole percent.

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